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04944748 **Image available**
RECORDED MATTER, PRODUCTION THEREOF AND RECORDING SHEET

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ABSTRACT

PURPOSE: To enhance the water resistance and durability of recorded matter by an ink jet printer and to keep high image quality for a long period of time.

CONSTITUTION: In a recording sheet wherein a base material 1, a porous alumina hydrate layer 2 and a porous high-polymer layer 3 are laminated, a dye is fixed to the porous alumina hydrate layer 2 through the porous high-polymer layer 3 by an ink jet printer to form an image and, thereafter, the porous-high polymer layer 3 is densified to form a transparent high-polymer film.

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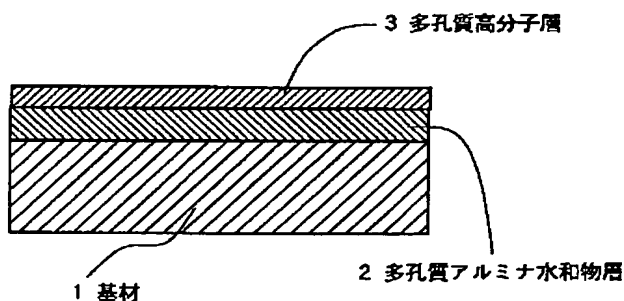
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(54) 【発明の名称】 記録物およびその製造方法および記録シート

(57) 【要約】

【目的】 インクジェットプリンターによる記録物の耐水性、耐久性を向上し、長期間、高画質を維持する。

【構成】 基材1、多孔質アルミナ水和物層2、多孔質高分子層3が積層された記録シートに、インクジェットプリンターで多孔質高分子層3を通して多孔質アルミナ水和物層2に色素を定着させて画像を形成した後、多孔質高分子層3を緻密化して透明高分子膜を形成する。



【特許請求の範囲】

【請求項1】基材上に、色素によって画像が形成された多孔質アルミナ水和物層を有し、該多孔質アルミナ水和物層が透明高分子膜で被覆された記録物。

【請求項2】透明高分子膜が、透明仕上りになる塗膜を形成する塗料を塗布乾燥して得られたものである請求項1の記録物。

【請求項3】透明高分子膜が、多孔質高分子を緻密化して得られたものである請求項1の記録物。

【請求項4】基材上に形成された多孔質アルミナ水和物層に、色素を定着させて画像を形成した後、該多孔質アルミナ水和物層に透明仕上りになる塗膜を形成する塗料を塗布乾燥して透明高分子膜を形成する記録物の製造方法。

【請求項5】基材上に形成された多孔質アルミナ水和物層の上に、さらに多孔質高分子層を形成し、多孔質高分子層を通して多孔質アルミナ水和物層に色素を定着させて画像を形成した後、多孔質高分子層を加熱処理することにより緻密化して多孔質アルミナ水和物層の上層に透明高分子膜を形成する記録物の製造方法。

【請求項6】多孔質高分子層を、高分子ラテックスを多孔質アルミナ水和物層に塗布乾燥することにより形成する請求項5の記録物の製造方法。

【請求項7】高分子ラテックスをシリカゾルと混合して塗布する請求項6の記録物の製造方法。

【請求項8】画像の形成にインクジェットプリンターを用いる請求項4～7いずれか1の記録物の製造方法。

【請求項9】基材上に形成された多孔質アルミナ水和物層の上に多孔質高分子層が形成されたインクジェットプリンター用の記録シート。

【請求項10】多孔質高分子層中に異種微粒子が分散している請求項9の記録シート。

【請求項11】多孔質高分子層が、高分子ラテックスの塗布乾燥物である請求項9または10の記録シート。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、記録物およびその製造方法および記録シートに関し、特にインクジェットプリンターに適する記録物およびその製造方法および記録シートに関するものである。

【0002】

【従来の技術】インクジェット方式、静電転写方式、昇華型熱転写方式などの記録方式を用いて画像、特にフルカラーの画像を形成する方法が急速に普及しつつある。このような方式での目標は、銀塩写真であり、特に、色再現性、画像密度、光沢、耐水性、耐候性などを、いかに銀塩写真に近づけるかが開発の課題になっている。

【0003】このうちインクジェット方式は、ノズルから高速で射出したインク液滴を、被記録材に付着させて記録する方式であり、フルカラー化が容易なことや印字

騒音が低いなどの特長を有する。この記録方式では、使用されるインクは多量の溶媒を含んでいるので、高色濃度を得るためには大量のインクを用いる必要がある。また、インク液滴は連続的に射出されるので、最初の液滴が吸収されないうちに次の液滴が射出されると、インク液滴が融合してインクのドットが接合するビーディング現象が生じて画像が乱れる。したがって、インクジェットプリンター用の記録媒体には、インク吸収容量が大きく、かつ、インクの吸収速度が高いことが要求される。

【0004】このため、普通の紙やフィルムでは十分な吸収性、発色性、解像度が得られないので、特開平2-276670号などのように、基材上にアルミナ水和物からなる多孔質層を設けた記録媒体が提案されている。このような記録媒体に、インクジェット方式で記録すると、インクの吸収性、定着性に優れ、解像度の高い画像が得られることが報告されている。

【0005】

【発明が解決しようとする課題】インクジェット方式では溶媒可溶性の色素により画像が形成されているので、記録物の耐水性、耐候性については必ずしも十分ではなく、屋外で長期間曝露されるような環境では、退色などの問題が発生するおそれがある。また、多孔質のインク受容層の場合、インク以外の成分を吸着して画像が汚れるおそれもある。本発明は、解像度、発色性が良好で、かつ、耐水性、耐候性、耐汚染性に優れた記録物を提供することを目的とする。

【0006】

【課題を解決するための手段】本発明は、基材上に、色素によって画像が形成された多孔質アルミナ水和物層を有し、該多孔質アルミナ水和物層が透明高分子膜で被覆された記録物を提供するものである。

【0007】基材としては特に限定されず、種々のものを使用することができる。具体的には、ポリエチレンテレフタレートなどのポリエステル、ポリカーボネート、ETFEなどのフッ素系樹脂など種々のプラスチック類や紙類を好適に使用することができる。さらに、ガラスや金属、あるいは天然皮革、人工皮革、布なども使用することができる。これらの基材には、多孔質アルミナ水和物の接着強度を向上させるなどの目的で、コロナ放電処理やアンダーコートなどの処理を行うこともできる。

【0008】基材として透明プラスチックフィルムなどを使用した場合には、OHP（オーバーヘッドプロジェクター）などにも使用できる透明な記録物が得られる。基材として、白色顔料を含んだ不透明プラスチックフィルムや、紙などを使用した場合には、銀塩写真に匹敵する記録物が得られる。また、人工皮革や布などにも色濃度が高く、細密な画像が形成できる。

【0009】多孔質アルミナ水和物は、アルミナ水和物をバインダーで結合した層として基材上に形成されている構成が好ましい。アルミナ水和物としては、ペーマイ

ト ($Al_2O_3 \cdot nH_2O$, $n=1 \sim 1.5$) が、吸水性が良好であるとともに、色素を選択的によく吸着するため、各種の記録方式を用いて、色濃度が高く鮮明な記録物が得られるので好ましい。

【0010】紙や布のように多孔性の基材表面に多孔質アルミナ水和物層が形成されている場合には、基材と多孔質アルミナ水和物層との間には、必ずしも明確な境界面がなくてもよい。すなわち、基材の表面付近にアルミナ水和物の多い部分があればよい。

【0011】多孔質アルミナ水和物は、その細孔構造が実質的に半径が $1 \sim 10$ nm の細孔からなり、細孔容積が $0.3 \sim 1.0$ cc/g である場合は、十分な吸水性を有しかつ透明性もあるので好ましい。このとき、基材が透明であれば、記録物も透明なものが得られる。基材が不透明である場合には、基材の質感を損なわずに必要なとされる吸水性などの物性を付与することが可能である。これらの物性に加え、多孔質アルミナ水和物の平均細孔半径が $3 \sim 7$ nm である場合はさらに好ましい。なお、細孔径分布の測定は、窒素吸脱着法による。

【0012】上記のような細孔構造を有する多孔質アルミナ水和物層を形成するには、アルミナゾルに、好ましくはバインダーを加えてスラリー状とし、ロールコーター、エアナイフコーター、ブレードコーター、ロッドコーター、バーコーター、コンマコーターなどを用いて基材上に塗布し、乾燥する方法を採用するのが好ましい。

【0013】バインダーとしては、でんぷんやその変性物、ポリビニルアルコールおよびその変性物、SBRラテックス、NBRラテックス、ヒドロキシセルロース、ポリビニルピロリドン等の有機物を用いることができる。バインダーの使用量は、少ないと多孔質アルミナ水和物層の強度が不十分になるおそれがあり、逆に多すぎるとインクの吸収量や色素の担持量が低くなるおそれがあるので、アルミナ水和物の $5 \sim 50$ 重量%程度が好ましい。

【0014】多孔質アルミナ水和物層の厚さは、薄すぎると色素を十分担持できず、色濃度の低い印刷物しか得られないおそれがあるので好ましくない。逆に厚すぎると多孔質層の強度が低下したり、あるいは透明性が減少して印刷物の透明性あるいは質感が損なわれるおそれがあるので好ましくない。多孔質アルミナ水和物層の好ましい厚さは、 $1 \sim 50 \mu m$ である。

【0015】本発明における透明高分子膜とは、上記多孔質アルミナ水和物層の表面に形成されこれを被覆する。この透明高分子膜は、画像の耐水性、耐候性を向上させる効果を有する。ここで透明とは、多孔質アルミナ水和物に形成された画像が、高分子膜を通して観察し得ることをいう。無色であることが好ましいが、意匠性を付与するために着色したものであってもよい。透明高分子膜の材質は特に限定されず、種々の高分子材料を用いることができる。また、透明性を損なわない範囲で、充

填材などが配合されていてもさしつかえない。

【0016】透明高分子膜の厚さは、 $0.5 \sim 30 \mu m$ が好ましい。透明高分子膜の厚さが $0.5 \mu m$ に満たない場合は、耐水性、耐候性向上の効果が十分でなく、また、干渉色の発現によって画質が低下するおそれがあるので好ましくない。透明高分子膜の厚さが $30 \mu m$ を超える場合は、それ以上、耐水性、耐候性向上の効果が増大しないばかりでなく、高分子膜の隠れにより画質が低下したり、高分子膜のはがれや、記録物のカールが発生するおそれがあるので好ましくない。透明高分子膜のより好ましい厚さは、 $2 \sim 10 \mu m$ である。

【0017】透明高分子膜を形成する手段の一例として、画像形成後に多孔質アルミナ水和物に、実質的に顔料成分を含まない塗料、すなわち、透明仕上がりになる塗料を塗布する方法が挙げられる。塗料としては、油性塗料、繊維系誘導体塗料、合成樹脂塗料、フッ素樹脂塗料など種々のものを使用することができる。特に、画像形成に水性インクを使用したものに対しては、画像を滲ませたりすることがない点で、油性塗料などの油性溶媒を使用する塗料が好ましい。

【0018】塗料中の樹脂成分は、 $3 \sim 30$ 重量%であることが好ましい。塗料中の樹脂成分が 3 重量%に満たない場合は、形成される透明高分子膜が薄く、耐水性、耐候性向上の効果が十分でなく、また、干渉色の発現による画質の低下を生ずるおそれがあるので好ましくない。逆に、塗料中の樹脂成分が 30 重量%を超える場合は、塗料の粘度が上昇して、均一な塗布が困難になるため、画質が低下するおそれがあるので好ましくない。特に、本発明の場合、多孔質表面に塗膜を形成するため、塗料中の溶媒が多孔質アルミナ水和物に吸収されて塗布時に粘度が上昇するので、樹脂成分が 30 重量%を超える場合に塗布が困難になる。

【0019】塗料の塗布方法は、刷毛塗り、スプレー塗り、ローラー塗りなど特に限定されない。乾燥は、自然乾燥でよく、必要に応じて加熱してもよい。

【0020】透明高分子膜の形成手段として、上記のような塗布法以外に、基材上の多孔質アルミナ水和物層上にあらかじめ多孔質高分子層を形成した記録シートを用い、インクジェットプリンターなどによって記録した後、多孔質高分子層を緻密化して多孔質アルミナ水和物層上に透明高分子膜を形成する方法を採用することもできる。このとき、インクは多孔質高分子層を通して多孔質アルミナ水和物まで浸透し、アルミナ水和物に定着されて画像を形成する。多孔質高分子層の緻密化の手段としては、加熱処理が好ましい。

【0021】この方法に用いる記録シートの一例を図1に示す。基材1には多孔質アルミナ水和物層2が形成されており、さらに多孔質高分子層3が積層される。このような記録シートを用いる場合は、記録後に塗料などを用いなくても透明高分子膜が形成した記録物を得られる

という利点がある。

【0022】多孔質高分子層は、多孔質アルミナ水和物層上に高分子ラテックスを塗布乾燥して形成するのが好ましい。高分子ラテックスとしては、PVCラテックス、SBRラテックス、NBRラテックスなどを単独で、あるいは混合して用いることができる。

【0023】高分子ラテックスは、平均粒子径0.05～0.5 μ mであることが好ましい。高分子ラテックスの平均粒子径が0.05 μ mに満たない場合は、インクの吸収性・透過性の良好な多孔質高分子層が形成されず、多孔質アルミナ水和物層に十分インクが浸透して定着されず、所望の画像が形成できない。高分子ラテックスの平均粒子径が0.5 μ mを超える場合は、インクのドットが不均一になり画像の低下が生ずるおそれがある。高分子ラテックスより好ましい平均粒子径は、0.08～0.3 μ mである。

【0024】高分子ラテックスの皮膜形成最低温度は、50～150℃の範囲にあることが好ましい。皮膜形成最低温度とは、高分子ラテックスの塗膜を加熱した際に、これを均一に皮膜化することのできる最低温度である。本発明においては、高分子ラテックスを塗布した後、多孔質高分子層にするために、緻密な皮膜とはならないが一定の機械的強度を持つ程度にはラテックス粒子が結合するような条件で加熱乾燥する必要がある。皮膜形成最低温度が50℃に満たない場合は、高分子ラテックスを塗布して乾燥する際に、緻密な皮膜となりやすく多孔質高分子層を得るのが困難で、これを防ごうとすると乾燥時間が長くなり、工業的でないので好ましくない。皮膜形成最低温度が150℃を超える場合は、画像形成後の熱処理温度を高くする必要があり、高分子の分解や着色の問題、基材あるいは色素の熱変性の問題があるので好ましくない。より好ましい皮膜形成最低温度は、65～130℃である。

【0025】多孔質高分子層の厚さは、0.1～10 μ mが好ましい。厚さが0.1 μ mに満たない場合は、皮膜化したときの耐水性耐候性向上の効果が十分でなく、かつ、干渉色の発現による画質の低下をきたすおそれがあるので好ましくない。厚さが10 μ mを超える場合は、インクの吸収性が低下したり、クラックが発生して皮膜化したときに画質が低下したり、耐水性耐候性向上の効果が発生しないおそれがあるので好ましくない。多孔質高分子層のより好ましい厚さは0.3～5 μ m、特に好ましくは0.5～3 μ mである。

【0026】高分子ラテックスの固形分濃度は特に制限されないが、1～50重量%の固形分濃度のラテックスを適宜使用することができる。なお、高分子ラテックスにはバインダー作用のある他の高分子成分を添加してもよい。

【0027】高分子ラテックスの塗布方法は、特に制限されず、ロールコーター、エアナイフコーター、プレー

ドコーター、ロッドコーター、バーコーター、グラビアコーターなどを使用することができる。乾燥は、使用する高分子ラテックスの皮膜形成最低温度以下の温度で行うことが好ましい。

【0028】このようにして形成された記録シートに、多孔質高分子層の上からインクジェットプリンターで画像を形成した場合、多孔質高分子層を通してインクがアルミナ水和物層まで到達する。アルミナ水和物は、インク中の色素の吸着性が高いので、画像は実質的にアルミナ水和物層の部分に形成される。この後、多孔質高分子層を熱処理などで緻密化すると、透明化してアルミナ水和物層に定着された色素の保護層として作用するようになる。熱処理は、ラテックスの皮膜形成最低温度以上であればよく、加熱手段は、特に制限されず、熱風やアイロンなどを採用することができる。

【0029】さらに、高分子多孔質層に異種微粒子が分散している場合は、インクジェットプリンターで記録した場合の耐ビーディング特性が著しく向上するので好ましい。微粒子として無機粒子が好ましく、具体的にはシリカ粒子が好適である。この微粒子は大きさと配合量が適切であれば、高分子多孔質層を緻密化したときに透明性を損なうことがない。

【0030】シリカ粒子を使用する場合、粒子の直径としては0.03～0.3 μ m程度が好適である。粒子直径が0.03 μ mに満たない場合は、上記効果が十分発現しないので好ましくない。粒子直径が0.3 μ mを超える場合は、高分子多孔質層を緻密化したときに、透明性が不足して画質を劣化させるおそれがあるので好ましくない。より好ましい粒子直径は0.05～0.1 μ mである。

【0031】シリカ粒子を使用する場合、高分子多孔質層における高分子とシリカ粒子の混合割合は、高分子とシリカ粒子の合計量に対してシリカ粒子が50重量%以下であることが好ましい。シリカ粒子が50重量%を超える場合は、記録後に緻密透明化するのが困難であるので好ましくない。より好ましい割合は、高分子とシリカ粒子の合計量に対してシリカ粒子が15～40重量%である。

【0032】シリカ粒子が均一に分散した構成の高分子多孔質層を得る方法としては、高分子ラテックスにシリカゾルを混合した塗工液を調整し、これをアルミナ水和物層の上に塗布乾燥する方法が好適である。この場合、シリカ粒子は高分子多孔質層の形成の際にクラックの発生を抑制する効果も有する。塗布方法などはラテックス単独の場合と同様なものを採用することができる。高分子多孔質層の厚さもラテックス単独の場合と同じでよい。

【0033】高分子ラテックスを塗布して多孔質高分子層を形成した場合、シリカなどの異種粒子を配合してもしなくても、緻密透明化する際に層の厚さはほとんど変

化しない。すなわち多孔質ではあるが細孔容積の小さい高分子層が形成されていると考えられる。このため加熱したときに粒子が容易に融着して透明化するものと考えられる。

【0034】透明高分子膜を形成することにより、記録物の光沢度は向上する。特に、基材として紙を使用した場合には、光沢度が向上することにより画質の向上もみられる。基材として平滑なプラスチックフィルムを使用した場合は、もともと良好な光沢を有するので、光沢度が高くなりすぎて、記録物の用途によっては逆に質感が悪くことがありうる。このような場合には、透明高分子膜に艶消し処理を施すこともできる。

【0035】本発明の記録物は、特にインクジェットプリンターを用いて記録する場合に好適であるが、色素を用いて記録する他の記録方式にも適用可能である。

【0036】

【作用】本発明において透明高分子膜は、多孔質アルミナ水和物を被覆することにより、色素が水に触れたり、空気中の酸素、オゾン、 NO_x と反応したり、あるいは揮発するのを防止し、さらに紫外線を遮蔽する機能を有する。基材が紙、布の場合のように空気等を透過するものであっても、色素はアルミナ水和物層の透明高分子膜側により多く定着されているので、同様に効果を発揮する。

【0037】

【実施例】

実施例1

アルミニウムアルコキシドの加水分解・解膠法で合成した固形分18重量%のアルミナゾル100gと、ポリビニルアルコール6.2重量%水溶液32gとを混合して塗工液とした。この塗工液をポリエチレンテレフタレートフィルム（白フィルム、125 μm 厚）上に、乾燥後の塗工厚さが30 μm になるようにバーコーターを用いて塗工した。これを乾燥後、140℃で熱処理して記録シートとした。

【0038】この記録シートに、インクジェットプリンター（キヤノン株式会社製CJ-10型）を用いて画像を形成した後、ウレタン系の合成樹脂塗料（関西ペイント株式会社製ウレタンニス）を石油系シンナーで樹脂分20重量%に希釈したものを刷毛により塗布し、自然乾燥して、厚さ約5 μm の透明高分子膜を形成し、記録物を得た。

【0039】実施例2

実施例1の記録シートに、同様にインクジェットプリンターで記録した後、ポリビニルブチラル樹脂5重量%のn-ブタノール溶液を塗料とし、実施例1と同様にして塗布乾燥して、厚さ約5 μm の透明高分子膜を形成し、記録物を得た。

【0040】実施例3

実施例1の記録シート上に、平均粒子直径0.1 μm で

固形分10重量%のPVCラテックス（日本ゼオン株式会社製、商品名G351）を、バーコーターを用いて乾燥時の厚さが2 μm になるように塗布し、60℃の雰囲気中で加熱乾燥し多孔質高分子膜を形成した。

【0041】この記録シートにインクジェットプリンター（アイリス社製）を用いて画像を形成した後、熱風（100℃）で熱処理することにより、多孔質高分子膜を緻密化して透明高分子膜を形成し、記録物を得た。透明高分子膜の厚さは2 μm であった。

【0042】実施例4

実施例1の記録シート上に、平均粒子直径0.12 μm で固形分5重量%のSBRラテックス（日本ゼオン株式会社製、商品名ニボールLX382）を、バーコーターを用いて乾燥時の厚さが1 μm になるように塗布し、90℃の雰囲気中で加熱乾燥し多孔質高分子膜を形成した。

【0043】この記録シートにインクジェットプリンター（アイリス社製）を用いて画像を形成した後、熱風（130℃）で熱処理することにより、多孔質高分子膜を緻密化して透明高分子膜を形成し、記録物を得た。透明高分子膜の厚さは1 μm であった。

【0044】実施例5

平均粒子直径0.12 μm で固形分5重量%のSBRラテックス（日本ゼオン株式会社製、商品名ニボールLX382）と平均粒子直径0.08 μm のシリカゾル（触媒化成工業株式会社製、商品名カタロイドSI-80P）を固形分重量比で80:20の割合で混合して、総固形分濃度10重量%の塗工液を調製した。この混合塗工液は、経時的に特に変化はみられず安定であった。この塗工液を、実施例1の記録シート上に、バーコーターを用いて乾燥時の厚さが1.5 μm になるように塗布し、90℃の雰囲気中で加熱乾燥し、シリカ粒子が含有された多孔質高分子膜を形成した。

【0045】この記録シートにインクジェットプリンター（アイリス社製）を用いて画像を形成した後、熱風（130℃）で熱処理することにより、多孔質高分子膜を緻密化して透明高分子膜を形成し、記録物を得た。透明高分子膜の厚さは1.5 μm であった。

【0046】印字例

これらの記録物について、耐水性および耐候性を次のようにして評価した。透明高分子膜を形成しない以外は同様にして得た記録物を比較例として、結果を表1に示す。耐水性は、記録物を静水中に1日浸漬し、まったく変化のないものを○、若干にじみのあるものを△、著しく画質が低下したものを×として評価した。耐候性は、記録物を室内に3ヶ月間曝露し、黒色記録部の変色度合い（退色：黒から褐色）について、まったく変化しないものを○、若干変色したものを△、褐色に変化したものを×として評価した。

【0047】

【表1】

	耐水性	耐候性
実施例1	○	○
実施例2	○	○
実施例3	○	○
実施例4	○	○
実施例5	○	○
比較例	△	×

れ、長期間にわたって高画質を維持する保存安定性を有する。特に、水性インクを用いた記録に対して好適である。また、本発明の記録方法は、記録物に好ましい光沢を付与することができるという効果も有する。

【図面の簡単な説明】

【図1】本発明の記録シートの1例の構成を示す説明図

【符号の説明】

1：基材

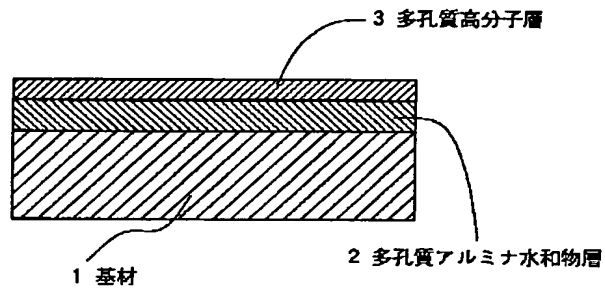
2：多孔質アルミナ水和物層

10 3：多孔質高分子層

【0048】

【発明の効果】本発明の記録物は、耐水性、耐候性に優

【図1】



PATENT ABSTRACTS OF JAPAN

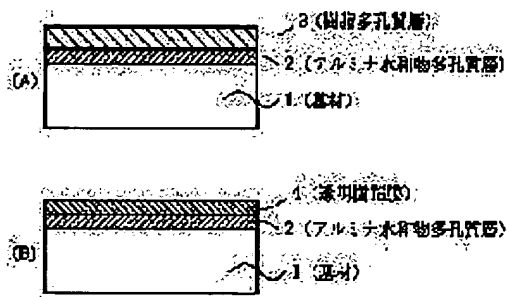
(11)Publication number : 08-002090
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(51)Int.Cl. B41M 5/00

(21)Application number : 06-139163 (71)Applicant : ASAHI GLASS CO LTD
(22)Date of filing : 21.06.1994 (72)Inventor : SUMITA KATSUTOSHI
KIJIMUTA HITOSHI

(54) INK JET RECORDING CARD, PRODUCTION THEREOF AND RECORDING MEDIUM

(57)Abstract:
PURPOSE: To provide a card recording a full-color image of high quality or character data. according to an ink jet system and excellent in abrasion resistance, antistaining properties, water resistance, weatherability and preservability.
CONSTITUTION: In the card like recording medium wherein a base material 1, an alumina hydrate porous layer 2 and a resin porous layer 3 are laminated, an image is formed on the alumina hydrate porous layer 2 through the resin porous layer 2 by an ink jet printer and, thereafter, the resin porous layer 3 is densified to form a transparent resin film 4.



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[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The ink-jet record type cards which have the hydrated-alumina porous layer by which a picture or alphabetic information was formed with the ink jet printer on the card-like base material, and have a transparent resin film on this hydrated-alumina porous layer

[Claim 2] The ink-jet record type cards according to claim 1 whose aforementioned hydrated alumina is a boehmite

[Claim 3] The ink-jet record type card according to claim 1 or 2 whose aforementioned transparent resin film is what is obtained by heat-treatment by precise-turning in a resin porous layer.

[Claim 4] The manufacture method of an ink-jet record type card of having the process which forms a picture or alphabetic information in the aforementioned hydrated-alumina porous layer of the record medium equipped with the hydrated-alumina porous layer prepared on the base material and the aforementioned base material, and the resin porous layer prepared on the aforementioned hydrated-alumina porous layer with an ink jet printer, and the process which turns precisely by heat-treating the aforementioned resin porous layer after that, and forms a transparent resin film on the aforementioned hydrated-alumina porous layer.

[Claim 5] The manufacture method of the ink-jet record type card according to claim 4 formed by the aforementioned resin porous layer's applying a resin latex, and drying.

[Claim 6] The manufacture method of an ink-jet record type card according to claim 4 or 5 that the aforementioned resin porous layer contains the metallic-oxide particle.

[Claim 7] The manufacture method of an ink-jet record type card according to claim 6 that the aforementioned metallic-oxide particle is a particle of a silica.

[Claim 8] The manufacture method of the ink-jet record type card according to claim 4 formed by the aforementioned resin porous layer's applying the mixture of a resin latex and a silica sol, and drying.

[Claim 9] The record medium of the ink-jet record type cards which have a hydrated-alumina porous layer on a base material, and have the resin porous layer which is ink permeability and can carry out the precise rarefaction by heat-treatment on this hydrated-alumina porous layer.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to ink-jet record type cards, the manufacture method of those, and its record medium.

[0002]

[Description of the Prior Art] Magnetic cards, such as a money card, a credit card, an ID card, a telephone card, an orange card, a commuter pass, and a bus card, etc. come to be widely used in large quantities with development of information processing technology, and it is just arrival of card society. Moreover, also in certificate cards, such as a personnel certificate and a membership card, it being full color and recording a photograph of his face etc. on a direct card is also increasing.

[0003] In such cards, if an individual picture and individual alphabetic information are easily recordable on a card face, it is effective in respect of improvement in reliability or operating efficiency. Moreover, in prepaid cards, such as a telephone card, for the design card with an eye on increase of the added value by the individual design besides the usual card and improvement in fashionability to begin to spread widely, and to be able to publish a design card from fewer number of sheets is desired.

Furthermore, the requests to full-color-izing are also mounting.

[0004] As the character to these card top, and a recording method of image information, printing technology is mainly used. Although printing technology is suitable when it is high, the cost at the time of extensive printing is a low and picture quality also records a finite character and finite image information so much, it is unsuitable for recording a character and image information on a small number of card individually. Moreover, abrasion resistance and resistance to contamination are required of the character and image information which were formed on the card, and the method which is wearing a front face by the bright film for the reason, the method of printing using ultraviolet-rays hardening ink, etc. are taken.

[0005] On the other hand, development of the method of recording speedily the individual image information to a small number of card is furthered with development of non impact record technology in recent years. For example, in the magnetic commuter pass, to record the individual information on denomination simultaneously with record to a magnetic surface for the increase in efficiency of ticketing is desired, and application of a non impact recording method is considered and put in practical use.

[0006] Thus, to put using and recording non impact record technology on a card medium in practical use, and to record not only alphabetic information but an individual full color picture about the content of record is desired.

[0007] As a non impact recording method, an ink-jet recording method, the electrophotography method, the electrostatic imprint method, the hot printing method, the sensible-heat method, etc. are examined. In this, especially an ink-jet recording method is a method which the ink drop injected at high speed is made to adhere to a record medium, and records it from a nozzle, and it has the features, like printing noise with easy full-color-izing is low.

[0008] In this ink-jet recording method, since the ink used contains a lot of solvents, in order to obtain the high depth of shade, it is necessary to use a lot of ink. Moreover, if the following drop is injected before the first drop is absorbed, since an ink drop is injected continuously, the beading phenomenon which an ink drop unites and the dot of ink joins will arise, and a picture will be confused. Therefore, it is required for the record medium for ink jet printers that the absorption capacity of ink should be large and the rate of absorption of ink should be high.

[0009] However, since neither absorptivity sufficient with ordinary paper and an ordinary film, coloring nature nor resolution is obtained, the record medium which prepared the porous layer which consists of a hydrated alumina on the base material like JP,2-276670,A is proposed. If it records on such a record medium by the ink-jet recording method, it excels in the absorptivity of ink, and the fixing nature of coloring matter, and it is reported that a picture with high resolution is acquired.

[0010]

[Problem(s) to be Solved by the Invention] However, in an ink-jet recording method, since a character and image information are formed with the coloring matter of aqueous solvent fusibility, about the water resistance of a record object, and weatherability, it is not necessarily enough, and there is a possibility that problems, such as fading, may occur, in an environment by which a long exposure is carried out outdoors. Moreover, there is also a possibility that a hydrated-alumina porous layer may adsorb components other than ink, and a picture may become dirty.

[0011] Furthermore, although a beautiful picture is formed at the beginning when it records on a hydrated-alumina porous layer by the ink-jet recording method, it may become dirty from prolonged use that it is an operating condition like especially a card. Moreover, the hydrated-alumina porous layer itself may be worn out.

[0012] The purpose of this invention has resolution and good coloring nature, and they are to offer the ink-jet record type cards

excellent in water resistance, weatherability, resistance to contamination, and abrasion resistance, and the manufacture method of those.

[0013]

[Means for Solving the Problem] According to this invention, the ink-jet record type cards which have the hydrated-alumina porous layer by which a picture or alphabetic information was formed with the ink jet printer on the card-like base material, and have a transparent resin film on this alumina hydration matter layer are offered.

[0014] Moreover, the manufacture method of an ink-jet record type card of having the process which forms a picture or alphabetic information in the aforementioned hydrated-alumina porous layer of the record medium which was equipped with the hydrated-alumina porous layer prepared on the base material and the aforementioned base material and the resin porous layer prepared on the aforementioned hydrated-alumina porous layer according to this invention with an ink jet printer, and the process which turn precisely and form a transparent resin film on the aforementioned hydrated-alumina porous layer by heat-treating the aforementioned resin porous layer after that is offered.

[0015] Moreover, according to this invention, it has a hydrated-alumina porous layer on a base material, and the record medium of the ink-jet record type cards which have the resin porous layer which is ink permeability and can carry out the precise rarefaction by heat-treatment on this hydrated-alumina porous layer is offered.

[0016] Although it is not limited but various things can be used especially as a base material used for this invention, plastics, such as paper currently used as a card material, and PVC (polyvinyl chloride), PET (polyethylene tele phthalate), is suitable. Corona discharge processing, under-coat processing, etc. can also be performed in these base materials for the purpose of raising the bond strength of a hydrated-alumina porous layer.

[0017] A hydrated-alumina porous layer has the desirable composition which combined the hydrated alumina with the binder. Since it often adsorbs coloring matter alternatively as a hydrated alumina while absorptivity of a boehmite (aluminum₂ O₃ and nH₂ O, n=1-1.5) is good, and a picture with it is acquired, it is desirable. [the high depth of shade and] [clear]

[0018] Since the pore structure consists of pore with a radius of 1-15nm substantially, and that pore volume is 0.3 - 1.0 cc/g has sufficient absorptivity and it is transparent, a hydrated-alumina porous layer is desirable. If the hydrated-alumina porous layer which has the pore structure of this range is used, physical properties needed, such as the absorptivity of ink, can be given without spoiling the texture of a base material. Moreover, it is still more desirable if the average pore radius of a hydrated-alumina porous layer is the range which is 3-7nm. In addition, measurement of a pore volume distribution is based on a nitrogen adsorption-and-desorption method.

[0019] In order to form the hydrated-alumina porous layer which has the above pore structures, a binder is preferably added to an alumina sol and it considers as the shape of a slurry, and it can apply on a base material using a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a comma coating machine, etc., and the method of drying can be adopted preferably.

[0020] As a binder used for a hydrated-alumina porous layer, the organic substance, such as starch, its denaturation object, polyvinyl alcohol and its denaturation object, an SBR (butadiene-styrenerubber) latex, an NBR (acrylonitrile butadiene rubber) latex, a hydroxy cellulose, and a polyvinyl pyrrolidone, can be used. Since it has a possibility that the intensity of a hydrated-alumina porous layer may become inadequate when there is little amount of the binder used, and it has a possibility that the absorbed dose of ink and the amount of support of coloring matter may become low when there is conversely, about 5 - 50% of the weight of its hydrated alumina is desirable. [too much]

[0021] If it is too thin, neither the absorbed dose of ink nor its amount of adsorption of coloring matter is enough, and since a possibility that only the low printed matter of the depth of shade may be obtained has the thickness of a hydrated-alumina porous layer, it is not desirable. Conversely, since the intensity of a porous layer falls or there is a possibility that transparency may decrease and the texture of a record object may be spoiled when too thick, it is not desirable. The thickness with a desirable hydrated-alumina porous layer is 1-50 micrometers.

[0022] The transparent resin film of this invention is formed on the above-mentioned hydrated-alumina porous layer, and covers a hydrated-alumina porous layer. This transparent resin film raises the water resistance of the picture formed in the hydrated-alumina porous layer, weatherability, and resistance to contamination, and also raises the abrasion resistance of a hydrated-alumina porous layer. Here, transparence means that the picture formed in the hydrated-alumina porous layer can observe through a resin film. Although it is desirable that it is colorlessness, you may color in order to give design nature.

[0023] After forming a picture in a hydrated-alumina porous layer with an ink jet printer as means forming of a transparent resin film using the record medium which formed the resin porous layer beforehand on the hydrated-alumina porous layer on a base material, the method of turning precisely and forming a transparent resin film on a hydrated-alumina porous layer is adopted by heat-treating a resin porous layer.

[0024] In addition, although how to apply a paint etc., dry on a hydrated-alumina porous layer, and cover a hydrated-alumina porous layer with a protection film is also considered as means forming of a transparent resin film after recording on a hydrated-alumina porous layer by the ink-jet recording method, it will become remarkable time and effort in this case.

[0025] As for a resin porous layer, it is desirable to apply and dry and to form a macromolecule latex on a hydrated-alumina porous layer. As a macromolecule latex, it is independent, or a PVC latex (salt villa tex), an SBR latex, an NBR latex, etc. can be mixed and used.

[0026] As for a macromolecule latex, it is desirable that a mean particle diameter is 0.05-0.5 micrometers. When the mean particle diameter of a macromolecule-latex does not fulfill 0.05 micrometers, the good-porous-layer-of-the absorptivity of ink and permeability is not formed, consequently enough, ink permeates, a hydrated-alumina porous layer is not fixed to it, and a desired

picture cannot be formed. When the mean particle diameter of a macromolecule latex exceeds 0.5 micrometers, the dot of ink becomes uneven and there is a possibility that deterioration of quality of image may arise. The more desirable mean particle diameter of a macromolecule latex is 0.08-0.3 micrometers.

[0027] As for the coat formation minimum temperature of a macromolecule latex, it is desirable that it is in the range of 50-150 degrees C. When the coat formation minimum temperature heats the paint film of a macromolecule latex, it is minimum temperature which can carry out [coat]-izing of this uniformly. In this invention, although it does not become a precise resin coat in order to make it a resin porous layer after applying a macromolecule latex, a grade with a fixed mechanical strength is expected to heat and dry on conditions which a latex particle combines.

[0028] When coat formation temperature does not fulfill 50 degrees C, in case a macromolecule latex is applied on a hydrated-alumina porous layer and it dries, it is easy to form a precise coat, if it is difficult to obtain a porous resin layer and it tends to prevent this, the drying time will become long, and since it is not industrial, it is not desirable. Since it is necessary to make high heat treatment temperature after image formation and there is a problem of disassembly of a resin, the problem of coloring, a base material, or the heat conversion of coloring matter when the coat formation minimum temperature exceeds 150 degrees C, it is not desirable. The more desirable coat formation minimum temperature is 55-130 degrees C.

[0029] A resin porous layer can also be made to contain a metallic-oxide particle. Thus, since the beading-proof property at the time of recording with an ink jet printer improves remarkably and resolution improves when the metallic-oxide particle is distributing to the resin porous layer, it is desirable. As a metallic-oxide particle, a silica particle is used preferably. If a silica particle is used, transparency can be maintained when a resin porous layer is precisely turned by heat-treatment.

[0030] In order to obtain the resin porous layer which the silica particle distributed, it is desirable to apply and dry and to form the mixture of a macromolecule latex and a silica sol on a hydrated-alumina porous layer. In this case, the effect to suppress also has that a crack generates a silica particle in the case of resin porous-layer formation. As for a silica sol, it is desirable that the mean particle diameter is 0.03 micrometers or more. It is because the good resin porous layer of the absorptivity of ink and permeability is not formed and a desired picture cannot be formed, when a mean particle diameter does not fulfill 0.03 micrometers.

[0031] As for the addition of a silica sol, it is desirable that it is 50 or less % of the weight at a solid-content equivalent weight rate to the resin in a porous layer. Since it is difficult to make it precise even if it heat-treats a resin porous layer when the addition of a silica sol exceeds 50 % of the weight, it is not desirable. The more desirable addition of a silica sol is 15 - 40 % of the weight at a solid-content equivalent weight rate.

[0032] The thickness of a resin porous layer has desirable 0.3-5 micrometers. when thickness does not fulfill 0.3 micrometers, the effect of the water resistance when coat-izing, weatherability, and contamination-resistant improvement is enough -- since there is a possibility of it not coming out and causing deterioration of the quality of image by the manifestation of the interference color, it is not desirable. Since the absorptivity of ink falls, or quality of image deteriorates when a crack occurred and coat-izes or there are water resistance, weatherability, and a possibility that the effect of contamination-resistant improvement may no longer be acquired when thickness exceeds 5 micrometers, it is not desirable. More desirable thickness is 0.5-3 micrometers. In addition, the same is said of the thickness of the resin porous layer which the silica particle distributed.

[0033] Although there is especially no limit about the solid content of a macromolecule latex, the latex of 2.5 - 50% of the weight of a solid content can be used suitably. In addition, to a latex, you may add other macromolecule components with a binder operation, for example, the low latex of the coat formation minimum temperature.

[0034] Especially the method of application of a macromolecule latex is not restricted, but can use a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a gravure coating machine, etc. In addition, the same is said of the method of application of the mixture of a macromolecule latex and a silica sol. Moreover, it is desirable to perform dryness at the temperature below the coat formation minimum temperature of the macromolecule latex to be used.

[0035] Thus, when a picture and alphabetic information are recorded on the record medium with which the hydrated-alumina porous layer and the resin porous layer were formed on the base material with the upper shell ink jet printer of a resin porous layer, an ink drop is first absorbed by the resin porous layer, and ink permeates to a hydrated-alumina porous layer through a resin porous layer gradually. Since the adsorptivity of a hydrated alumina of the coloring matter in ink is high, a hydrated-alumina porous layer is adsorbed alternatively and the coloring matter in ink discovers the high depth of shade. Thus, a picture and alphabetic information are substantially formed in a hydrated-alumina porous layer.

[0036] Then, if it is made precise by heat-treating a resin porous layer, a resin porous layer will come to act as a protective coat of the coloring matter to which the transparent coat was formed and the hydrated-alumina porous layer was fixed. That what is necessary is just to perform heat treatment at the temperature more than the coat formation minimum temperature of a macromolecule latex, especially a heating means is not restricted but hot blast, an iron, a heating roller, etc. can be used for it.

[0037] Water resistance, weatherability, and the resistance to contamination and abrasion resistance of a recording surface not only improve, but glossiness improves by forming a transparent resin film. Especially when glossiness improves and paper is used as a base material, improvement in quality of image is found. Moreover, when glossiness becomes high too much conversely and texture becomes bad like [when plastic SUTCHIKU smooth as a base material is used for example,], lusterless processing can also be performed to a transparent resin film.

[0038] When the record medium with which the hydrated-alumina porous layer and the resin porous layer were formed on the base material is larger than a card After forming a transparent resin film by heat-treatment, you may cut a record medium on each card. After forming a picture in a hydrated-alumina porous layer with an ink jet printer, a record medium may be cut in the size of each card, and a transparent resin film may be formed for every card by the afterbaking processing. The record medium with

which the hydrated-alumina porous layer and the resin porous layer were formed on the base material is first cut in the size of each card. Then, after forming a picture in the hydrated-alumina porous layer of each card with an ink jet printer, with heat treatment, a transparent resin film may be formed and it can choose suitably according to the kind of card, its presswork, etc. [0039] As cards to which this invention is applied, magnetic cards, such as certificate cards, such as a card, a personnel certificate, and a membership card, a money card, a credit card, an ID card, a telephone card, an orange card, a commuter pass, and a bus card, etc. are mentioned suitably.

[0040] An example of the ink-jet record type cards to which this invention is applied is shown in drawing 1. First, as shown in drawing 1 (A), the hydrated-alumina porous layer 2 is formed on a base material 1, next the resin porous layer 3 is formed on the hydrated-alumina porous layer 2, and a record medium is created. Then, a picture is formed in the hydrated-alumina porous layer 2 through the resin porous layer 3 with an ink jet printer. Next, as shown in drawing 1 (B), it heat-treats, the resin porous layer 3 is turned precisely, and the transparent resin film 4 is formed. Thus, the cards in which the transparent resin film 5 was formed even if it did not use a paint etc. after record, when the record medium with which the resin porous layer 3 was formed beforehand was used are obtained.

[0041] Drawing 2 is a cross section for explaining other examples of the ink-jet record type cards to which this invention is applied. This example is the case where this invention is applied to magnetic cards, such as a money card, a credit card, an ID card, a telephone card, an orange card, a commuter pass, and a bus card. First, as shown in drawing 2 (A), the hydrated-alumina porous layer 2 is formed on the front face of the base material 1 which has a magnetic layer 4 at the rear face, next the resin porous layer 3 is formed on the hydrated-alumina porous layer 2, and a record medium is created. Then, a picture is formed in the hydrated-alumina porous layer 2 through the resin porous layer 3 with an ink jet printer. Next, as shown in drawing 2 (B), it heat-treats, the resin porous layer 3 is turned precisely, and the transparent resin film 4 is formed.

[0042]

[Function] In this invention, by forming a hydrated-alumina porous layer and a resin porous layer in a card side, it has the function which is full color and can record a quality picture and quality alphabetic information with an ink jet printer, and further, by heat-treating a resin porous layer, when it turns precisely and a transparent resin film covers a hydrated-alumina porous layer, the abrasion resistance of a card side, contamination-resistant improvement, and improvement in the shelf life of the recorded picture or alphabetic information can be aimed at easily simple.

[0043]

[Example]

32g of 6.2 % of the weight solution of polyvinyl alcohol was mixed with alumina-sol of 18 % of the weight of solid contents compounded by hydrolysis and amalgam-decomposition method of example 1 aluminum alkoxide 100g, and it considered as coating liquid. The amount of coating after dryness is this coating liquid on the polyethylene-terephthalate film (a white film, 175-micrometer **) of A4 size 30 g/m2 Coating was carried out using the bar coating machine so that it might become. It heat-treated at 140 degrees C after dryness, and the sheet with which the hydrated-alumina porous layer was formed was obtained. Furthermore, on this sheet, it applied so that the SBR latex (Nippon Zeon Co., Ltd., tradename Nipol LX382) of 10 % of the weight of solid contents and a bar coating machine might be used and the thickness at the time of dryness might be set to 1.5 micrometers, and it dried at 70 degrees C, and the record medium was obtained.

[0044] The ink jet printer (iris company make) was used for this record medium, after recording beforehand the full color picture which read a photograph of his face and alphabetic information into card size, it heat-treated by hot blast (130 degrees C), the precise rarefaction of the resin porous layer was carried out, it judged in card size after that, and ink-jet record type cards were obtained. The ink-jet record type cards of this example have resolution and good coloring nature, and they were excellent in water resistance, weatherability, resistance to contamination, and abrasion resistance.

[0045] The same coating liquid as example 2 example 1 is used, and the amount of coating at the time of dryness is 20 g/m2 on a white telephone card. It applied using the bar coating machine so that it might become, and it heat-treated at 140 degrees C after dryness. Furthermore, the mixture (the solid-content weight ratio 8:2, 10 % of the weight) of the SBR latex and sill KAZORU (KATAROIDO S1 made from Catalyst Chemicals Industry -80 P) which were used in the example 1 was applied so that the thickness at the time of dryness might be set to 2 micrometers, and it dried at 80 degrees C.

[0046] After recording a full color picture on this card medium with an ink jet printer (iris company make), it heat-treated by hot blast (130 degrees C), and the precise rarefaction of the resin porous layer containing a silica particle was carried out, and the test card of a telephone card was created. The telephone card of this example has resolution and good coloring nature, and they were excellent in water resistance, weatherability, resistance to contamination, and abrasion resistance.

[0047]

[Effect of the Invention] In the ink-jet record type cards of this invention, by recording quality and full color a picture and alphabetic information by the ink-jet recording method, the added value and fashionability by the individual design can be raised, and it can publish from fewer number of sheets. Moreover, abrasion resistance and resistance to contamination are given by formation of a transparent resin film outside water resistance and weatherability. Furthermore, the ink-jet record type cards of this invention can be formed easily simple by precise-turning and forming this transparent resin film by heat-treating a resin porous layer.

[Translation done.]

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MEANS

[Means for Solving the Problem] According to this invention, the ink-jet record type cards which have the hydrated-alumina porous layer by which a picture or alphabetic information was formed with the ink jet printer on the card-like base material, and have a transparent resin film on this alumina hydration matter layer are offered.

[0014] Moreover, the manufacture method of an ink-jet record type card of having the process which forms a picture or alphabetic information in the aforementioned hydrated-alumina porous layer of the record medium which was equipped with the hydrated-alumina porous layer prepared on the base material and the aforementioned base material and the resin porous layer prepared on the aforementioned hydrated-alumina porous layer according to this invention with an ink jet printer, and the process which turn precisely and form a transparent resin film on the aforementioned hydrated-alumina porous layer by heat-treating the aforementioned resin porous layer after that is offered.

[0015] Moreover, according to this invention, it has a hydrated-alumina porous layer on a base material, and the record medium of the ink-jet record type cards which have the resin porous layer which is ink permeability and can carry out the precise rarefaction by heat-treatment on this hydrated-alumina porous layer is offered.

[0016] Although it is not limited but various things can be used especially as a base material used for this invention, plastics, such as paper currently used as a card material, and PVC (polyvinyl chloride), PET (polyethylene tele phthalate), is suitable. Corona discharge processing, under-coat processing, etc. can also be performed in these base materials for the purpose of raising the bond strength of a hydrated-alumina porous layer.

[0017] A hydrated-alumina porous layer has the desirable composition which combined the hydrated alumina with the binder. Since it often adsorbs coloring matter alternatively as a hydrated alumina while absorptivity of a boehmite (aluminum₂ O₃ and nH₂ O, n=1-1.5) is good, and a picture with it is acquired, it is desirable. [the high depth of shade and] [clear]

[0018] Since the pore structure consists of pore with a radius of 1-15nm substantially, and that pore volume is 0.3 - 1.0 cc/g has sufficient absorptivity and it is transparent, a hydrated-alumina porous layer is desirable. If the hydrated-alumina porous layer which has the pore structure of this range is used, physical properties needed, such as the absorptivity of ink, can be given without spoiling the texture of a base material. Moreover, it is still more desirable if the average pore radius of a hydrated-alumina porous layer is the range which is 3-7nm. In addition, measurement of a pore volume distribution is based on a nitrogen adsorption-and-desorption method.

[0019] In order to form the hydrated-alumina porous layer which has the above pore structures, a binder is preferably added to an alumina sol and it considers as the shape of a slurry, and it can apply on a base material using a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a comma coating machine, etc., and the method of drying can be adopted preferably.

[0020] As a binder used for a hydrated-alumina porous layer, the organic substance, such as starch, its denaturation object, polyvinyl alcohol and its denaturation object, an SBR (butadiene-styrenerubber) latex, an NBR (acrylonitrile butadiene rubber) latex, a hydroxy cellulose, and a polyvinyl pyrrolidone, can be used. Since it has a possibility that the intensity of a hydrated-alumina porous layer may become inadequate when there is little amount of the binder used, and it has a possibility that the absorbed dose of ink and the amount of support of coloring matter may become low when there is conversely, about 5 - 50% of the weight of its hydrated alumina is desirable. [too much]

[0021] If it is too thin, neither the absorbed dose of ink nor its amount of adsorption of coloring matter is enough, and since a possibility that only the low printed matter of the depth of shade may be obtained has the thickness of a hydrated-alumina porous layer, it is not desirable. Conversely, since the intensity of a porous layer falls or there is a possibility that transparency may decrease and the texture of a record object may be spoiled when too thick, it is not desirable. The thickness with a desirable hydrated-alumina porous layer is 1-50 micrometers.

[0022] The transparent resin film of this invention is formed on the above-mentioned hydrated-alumina porous layer, and covers a hydrated-alumina porous layer. This transparent resin film raises the water resistance of the picture formed in the hydrated-alumina porous layer, weatherability, and resistance to contamination, and also raises the abrasion resistance of a hydrated-alumina porous layer. Here, transparency means that the picture formed in the hydrated-alumina porous layer can observe through a resin film. Although it is desirable that it is colorlessness, you may color in order to give design nature.

[0023] After forming a picture in a hydrated-alumina porous layer with an ink jet printer as means forming of a transparent resin film using the record medium which formed the resin porous layer beforehand on the hydrated-alumina porous layer on a base material, the method of turning precisely and forming a transparent resin film on a hydrated-alumina porous layer is adopted by heat-treating a resin porous layer.

[0024] In addition, although how to apply a paint etc., dry on a hydrated-alumina porous layer, and cover a hydrated-alumina porous layer with a protection film is also considered as means forming of a transparent resin film after recording on a hydrated-alumina porous layer by the ink-jet recording method, it will become remarkable time and effort in this case.

[0025] As for a resin porous layer, it is desirable to apply and dry and to form a macromolecule latex on a hydrated-alumina porous layer. As a macromolecule latex, it is independent, or a PVC latex (salt villa tex), an SBR latex, an NBR latex, etc. can be mixed and used.

[0026] As for a macromolecule latex, it is desirable that a mean particle diameter is 0.05-0.5 micrometers. When the mean particle diameter of a macromolecule latex does not fulfill 0.05 micrometers, the good porous layer of the absorptivity of ink and permeability is not formed, consequently enough, ink permeates, a hydrated-alumina porous layer is not fixed to it, and a desired picture cannot be formed. When the mean particle diameter of a macromolecule latex exceeds 0.5 micrometers, the dot of ink becomes uneven and there is a possibility that deterioration of quality of image may arise. The more desirable mean particle diameter of a macromolecule latex is 0.08-0.3 micrometers.

[0027] As for the coat formation minimum temperature of a macromolecule latex, it is desirable that it is in the range of 50-150 degrees C. When the coat formation minimum temperature heats the paint film of a macromolecule latex, it is minimum temperature which can carry out [coat]-izing of this uniformly. In this invention, although it does not become a precise resin coat in order to make it a resin porous layer after applying a macromolecule latex, a grade with a fixed mechanical strength is expected to heat and dry on conditions which a latex particle combines.

[0028] When coat formation temperature does not fulfill 50 degrees C, in case a macromolecule latex is applied on a hydrated-alumina porous layer and it dries, it is easy to form a precise coat, if it is difficult to obtain a porous resin layer and it tends to prevent this, the drying time will become long, and since it is not industrial, it is not desirable. Since it is necessary to make high heat treatment temperature after image formation and there is a problem of disassembly of a resin, the problem of coloring, a base material, or the heat conversion of coloring matter when the coat formation minimum temperature exceeds 150 degrees C, it is not desirable. The more desirable coat formation minimum temperature is 55-130 degrees C.

[0029] A resin porous layer can also be made to contain a metallic-oxide particle. Thus, since the beading-proof property at the time of recording with an ink jet printer improves remarkably and resolution improves when the metallic-oxide particle is distributing to the resin porous layer, it is desirable. As a metallic-oxide particle, a silica particle is used preferably. If a silica particle is used, transparency can be maintained when a resin porous layer is precisely turned by heat-treatment.

[0030] In order to obtain the resin porous layer which the silica particle distributed, it is desirable to apply and dry and to form the mixture of a macromolecule latex and a silica sol on a hydrated-alumina porous layer. In this case, the effect to suppress also has that a crack generates a silica particle in the case of resin porous-layer formation. As for a silica sol, it is desirable that the mean particle diameter is 0.03 micrometers or more. It is because the good resin porous layer of the absorptivity of ink and permeability is not formed and a desired picture cannot be formed, when a mean particle diameter does not fulfill 0.03 micrometers.

[0031] As for the addition of a silica sol, it is desirable that it is 50 or less % of the weight at a solid-content equivalent weight rate to the resin in a porous layer. Since it is difficult to make it precise even if it heat-treats a resin porous layer when the addition of a silica sol exceeds 50 % of the weight, it is not desirable. The more desirable addition of a silica sol is 15 - 40 % of the weight at a solid-content equivalent weight rate.

[0032] The thickness of a resin porous layer has desirable 0.3-5 micrometers. when thickness does not fulfill 0.3 micrometers, the effect of the water resistance when coat-izing, weatherability, and contamination-resistant improvement is enough -- since there is a possibility of it not coming out and causing deterioration of the quality of image by the manifestation of the interference color, it is not desirable. Since the absorptivity of ink falls, or quality of image deteriorates when a crack occurred and coat-izes or there are water resistance, weatherability, and a possibility that the effect of contamination-resistant improvement may no longer be acquired when thickness exceeds 5 micrometers, it is not desirable. More desirable thickness is 0.5-3 micrometers. In addition, the same is said of the thickness of the resin porous layer which the silica particle distributed.

[0033] Although there is especially no limit about the solid content of a macromolecule latex, the latex of 2.5 - 50% of the weight of a solid content can be used suitably. In addition, to a latex, you may add other macromolecule components with a binder operation, for example, the low latex of the coat formation minimum temperature.

[0034] Especially the method of application of a macromolecule latex is not restricted, but can use a roll coater, an air knife coater, a blade coating machine, a rod coating machine, a bar coating machine, a gravure coating machine, etc. In addition, the same is said of the method of application of the mixture of a macromolecule latex and a silica sol. Moreover, it is desirable to perform dryness at the temperature below the coat formation minimum temperature of the macromolecule latex to be used.

[0035] Thus, when a picture and alphabetic information are recorded on the record medium with which the hydrated-alumina porous layer and the resin porous layer were formed on the base material with the upper shell ink jet printer of a resin porous layer, an ink drop is first absorbed by the resin porous layer, and ink permeates to a hydrated-alumina porous layer through a resin porous layer gradually. Since the adsorptivity of a hydrated alumina of the coloring matter in ink is high, a hydrated-alumina porous layer is adsorbed alternatively and the coloring matter in ink discovers the high depth of shade. Thus, a picture and alphabetic information are substantially formed in a hydrated-alumina porous layer.

[0036] Then, if it is made precise by heat-treating a resin porous layer, a resin porous layer will come to act as a protective coat of the coloring matter to which the transparent coat was formed and the hydrated-alumina porous layer was fixed. That what is necessary is just to perform heat treatment at the temperature more than the coat formation minimum temperature of a macromolecule latex, especially a heating means is not restricted but hot blast, an iron, a heating roller, etc. can be used for it.

[0037] Water resistance, weatherability, and the resistance to contamination and abrasion resistance of a recording surface not only improve, but glossiness improves by forming a transparent resin film. Especially when glossiness improves and paper is used as a base material, improvement in quality of image is found. Moreover, when glossiness becomes high too much conversely and texture becomes bad like [when plastic SUTCHIKKU smooth as a base material is used for example,], lusterless processing can also be performed to a transparent resin film.

[0038] When the record medium with which the hydrated-alumina porous layer and the resin porous layer were formed on the base material is larger than a card After forming a transparent resin film by heat-treatment, you may cut a record medium on each card. After forming a picture in a hydrated-alumina porous layer with an ink jet printer, a record medium may be cut in the size of each card, and a transparent resin film may be formed for every card by the afterbaking processing. The record medium with which the hydrated-alumina porous layer and the resin porous layer were formed on the base material is first cut in the size of each card. Then, after forming a picture in the hydrated-alumina porous layer of each card with an ink jet printer, with heat treatment, a transparent resin film may be formed and it can choose suitably according to the kind of card, its presswork, etc.

[0039] As cards to which this invention is applied, magnetic cards, such as certificate cards, such as a card, a personnel certificate, and a membership card, a money card, a credit card, an ID card, a telephone card, an orange card, a commuter pass, and a bus card, etc. are mentioned suitably.

[0040] An example of the ink-jet record type cards to which this invention is applied is shown in drawing 1 . First, as shown in drawing 1 (A), the hydrated-alumina porous layer 2 is formed on a base material 1, next the resin porous layer 3 is formed on the hydrated-alumina porous layer 2, and a record medium is created. Then, a picture is formed in the hydrated-alumina porous layer 2 through the resin porous layer 3 with an ink jet printer. Next, as shown in drawing 1 (B), it heat-treats, the resin porous layer 3 is turned precisely, and the transparent resin film 4 is formed. Thus, the cards in which the transparent resin film 5 was formed even if it did not use a paint etc. after record, when the record medium with which the resin porous layer 3 was formed beforehand was used are obtained.

[0041] Drawing 2 is a cross section for explaining other examples of the ink-jet record type cards to which this invention is applied. This example is the case where this invention is applied to magnetic cards, such as a money card, a credit card, an ID card, a telephone card, an orange card, a commuter pass, and a bus card. First, as shown in drawing 2 (A), the hydrated-alumina porous layer 2 is formed on the front face of the base material 1 which has a magnetic layer 4 at the rear face, next the resin porous layer 3 is formed on the hydrated-alumina porous layer 2, and a record medium is created. Then, a picture is formed in the hydrated-alumina porous layer 2 through the resin porous layer 3 with an ink jet printer. Next, as shown in drawing 2 (B), it heat-treats, the resin porous layer 3 is turned precisely, and the transparent resin film 4 is formed.

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OPERATION

[Function] It is an ink jet printer by forming a hydrated-alumina porous layer and a resin porous layer in a card side in this invention. It has the function which is full color and can record a quality picture and quality alphabetic information, and further, by heat-treating a resin porous layer, when it turns precisely and a transparent resin film covers a hydrated-alumina porous layer, the abrasion resistance of a card side, contamination-resistant improvement, and improvement in the shelf life of the recorded picture or alphabetic information can be aimed at easily simple.

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EXAMPLE

[Example]

32g of 6.2 % of the weight solution of polyvinyl alcohol was mixed with alumina-sol of 18 % of the weight of solid contents compounded by hydrolysis and amalgam-decomposition method of example 1 aluminum alkoxide 100g, and it considered as coating liquid. The amount of coating after dryness is this coating liquid on the polyethylene-terephthalate film (a white film, 175-micrometer **) of A4 size 30 g/m2 Coating was carried out using the bar coating machine so that it might become. It heat-treated at 140 degrees C after dryness, and the sheet with which the hydrated-alumina porous layer was formed was obtained. Furthermore, on this sheet, it applied so that the SBR latex (Nippon Zeon Co., Ltd., tradename Nipol LX382) of 10 % of the weight of solid contents and a bar coating machine might be used and the thickness at the time of dryness might be set to 1.5 micrometers, and it dried at 70 degrees C, and the record medium was obtained.

[0044] The ink jet printer (iris company make) was used for this record medium, after recording beforehand the full color picture which read a photograph of his face and alphabetic information into card size, it heat-treated by hot blast (130 degrees C), the resin porous layer was formed into precise transparence, it judged in card size after that, and ink-jet record type cards were obtained. The ink-jet record type cards of this example have resolution and good coloring nature, and they were excellent in water resistance, weatherability, resistance to contamination, and abrasion resistance.

[0045] The same coating liquid as example 2 example 1 is used, and the amount of coating at the time of dryness is 20 g/m2 on a white telephone card. It applied using the bar coating machine so that it might become, and it heat-treated at 140 degrees C after dryness. Furthermore, the mixture (the solid-content weight ratio 8:2, 10 % of the weight) of the SBR latex and sill KAZORU (KATAROIDO S1 made from Catalyst Chemicals Industry -80 P) which were used in the example 1 was applied so that the thickness at the time of dryness might be set to 2 micrometers, and it dried at 80 degrees C.

[0046] After recording a full color picture on this card medium with an ink jet printer (iris company make), it heat-treated by hot blast (130 degrees C), and the resin porous layer containing a silica particle was formed into precise transparence, and the test card of a telephone card was created. The telephone card of this example has resolution and good coloring nature, and they were excellent in water resistance, weatherability, resistance to contamination, and abrasion resistance.

[Translation done.]